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The Preparation of Cyclic Organic Carbonyl Compounds from η5-Cyclopentadienyltetracarbonylvanadium and Substituted Acetylenes

Ronald C. Newbold
Union College - Schenectady, NY

THE PREPARATION OF CYCLIC ORGANIC CARBONYL COMPOUNDS FROM η^5-CYCLOPENTADIENYLTETRACARBONYLVANADIUM AND SUBSTITUTED ACETYLENES

by

RONALD C. NEWBOLD

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ABSTRACT

NEWBOLD, RONALD The Preparation of Cyclic Organic Carbonyl Compounds from η^5-Cyclopentadienyltetracarbonylvanadium and Substituted Acetylenes. Department of Chemistry, June 1984.

Studies on the reactivity of many transition metal carbonyl complexes with various acetylenes have generated significant interest in the field of organometallic chemistry, but little effort has been put forth to make use of these compounds as genuine organic reagents. Most metal carbonyl compounds generate both organic and organometallic products, where oxidative cleavage becomes necessary to obtain the organic moiety. $(\eta^5\text{-}C_5H_5)V(CO)_4$ is an oxygen-sensitive carbonyl complex which has been shown to thermally react with bis-(pentafluorophenyl)acetylene to produce cyclic carbonyl compounds in high yield, particularly the quinone derivative, with few organometallic products. The thermal reactivity of $(\eta^5\text{-}C_5H_5)V(CO)_4$ is characterized with various symmetrically and non-symmetrically substituted acetylenes, with emphasis placed on the effect of electron-donating and withdrawing substituents on the alkyne. It was found that in general, acetylenes with electron-donating substituents such as 3-hexyne, bis-(trimethylsilyl)acetylene, and 2-butyne-1,4-diol will not react with $(\eta^5\text{-}C_5H_5)V(CO)_4$ to form organic carbonyl compounds. Acetylenes with electron-withdrawing substituents were found to react readily with this vanadium compound to form a variety of cyclic structures, including cyclopentadienones, quinones, tropones, and substituted benzene derivatives. Acetylenes in this catagory include dimethylacetylene

dicarboxylate, diphenylacetylene, and pentafluorophenyl phenyl acetylene. Catalytic activity is suggested in certain instances for η^5-cyclopentadienyltetracarbonylvanadium.

ACKNOWLEDGEMENTS

I would like to sincerely thank Dr. Donald Foust for all the invaluable experience and guidance he has given me. Professor Foust, I wish you all the best!

To all my friends at Union, you have truly made these past four years many of my finest. It shall not be the work I have completed which I will remember most, but the memories you all have given me.

Most importantly of all, I want to express my love and appreciation to my parents, for everything they have done. Without them, I would have accomplished little. Thanks!

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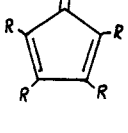
INTRODUCTION

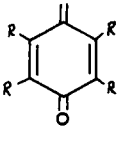
As early as 1938 it was discovered that basic solutions of iron carbonyl hydride [$H_2Fe(CO)_4$] produce hydroquinones when treated with acetylene at moderate temperatures.(1) This first research on the condensation of carbon monoxide and acetylene took place in Germany during World war II, and since that time a great deal of work has transpired in an effort to fully characterize the usefulness of the reaction between many transition metal carbonyl compounds and various acetylenes. Although the discovery of the high reactivity of the acetylenes and CO (in the presence of transition metals) drove those early scientists to study such reactions, nearly all their efforts were focused on the "novelty" of the new organometallic reagents and products. Relatively little effort was afforded to the study of their use a genuine reagents in the synthesis of organic compounds.

Unlike olefins, acetylenes react with carbon monoxide in the presence of metal carbonyl complexes to form a raft of compounds, both organic and organometallic in nature.(2) Examples of the possible products from such reactions include substituted cyclopentadeinones, quinones, tropones, and benzene derivatives, as well as five- and six-membered ring ketones.(3-5 and references therein) These compounds are illustrated in Figure 1.

In most cases, the outcome of a particular reaction is dependent not only upon the particular transition metal carbonyl chosen, but also upon the acetylene and specific reaction conditions, as alterations in any one of these parameters can significantly change

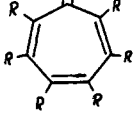


Cyclopenta-
dienone
(I)



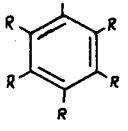
Quinone

(II)



Tropone

(III)



Substituted
Benzene
(IV)

Figure 1

the resulting products.(5-8) Research completed by R.S. Dickson and co-workers illustrates how changes in metal carbonyl compounds and acetylenic substituents can alter the distribution of organic products. Their work on carbonyl complexes of cobalt, rhodium and iridium with variously substituted acetylenes concludes that not only are the metal and the substituents on the alkyne influential on the nature and range of products formed, but that the bulkiness and electronegativity of those same substituents may play a decisive role in reaction results.

The scientist must be aware that although a specific metal carbonyl derivative may not react with certain acetylenes under particular conditions, optimum conditions may produce a myriad of products from a single-step reaction! An example of this comes from the work of W. Hubel and E.H. Braye, in which triiron dodecacarbonyl, $Fe_3(CO)_{12}$, was allowed to react with diphenylacetylene in petroleum ether at 90°C to yield up to twenty distinguishable products.(9) This type of reactivity opens new avenues to the organic chemist, since previously

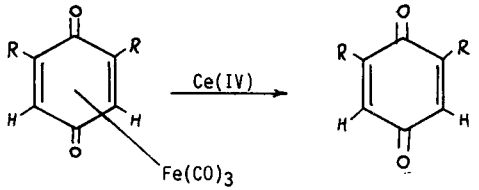
complex syntheses may now be replaced by the appropriate reaction(s) of metal carbonyl complexes and acetylenes to generate the desired organic targets.

A considerable amount of time and effort has gone into the study of these organometallic reactions, however nearly all have focused on metals in the latter half of the transition series', with little attention directed toward vanadium. A few studies have been conducted on reactions of aceytlene derivatives and the vanadium carbonyl η^5-cyclopentadienyltetracarbonylvanadium, $[(\eta^5\text{-}C_5H_5)V(CO)_4]$, or $CpV(CO)_4$, where most of this work concentrated on the photochemistry of such reactions, little concerned for possible application to synthetic preparations. (4)

This paper shall focus specifically on the thermal reactivity of $CpV(CO)_4$ with different symmetrically and non-symmetrically disubstituted acetylenes in application toward the synthesis of cyclic organic compounds in one-step processes. This oxygen-sensitive carbonyl compound has been found to generate high yields of cyclic carbonyl derivatives (especially quinones), and unlike most other transition metals, vanadium leaves few organometallic products.(4,10-13) Generally speaking, only syntheses giving rise to organic carbonyl compounds from acetylenic substrates and $CpV(CO)_4$ shall be discussed. The synthesis of organometallic products, or organic compounds containing no CO linkages, will not be treated here, but shall be left for future research.

As discussed in earlier works, metal carbonyl compounds are able to associate two of more molecules of the acetylenic substrates, with or without carbon monoxide (CO), into more complex organic moieties.

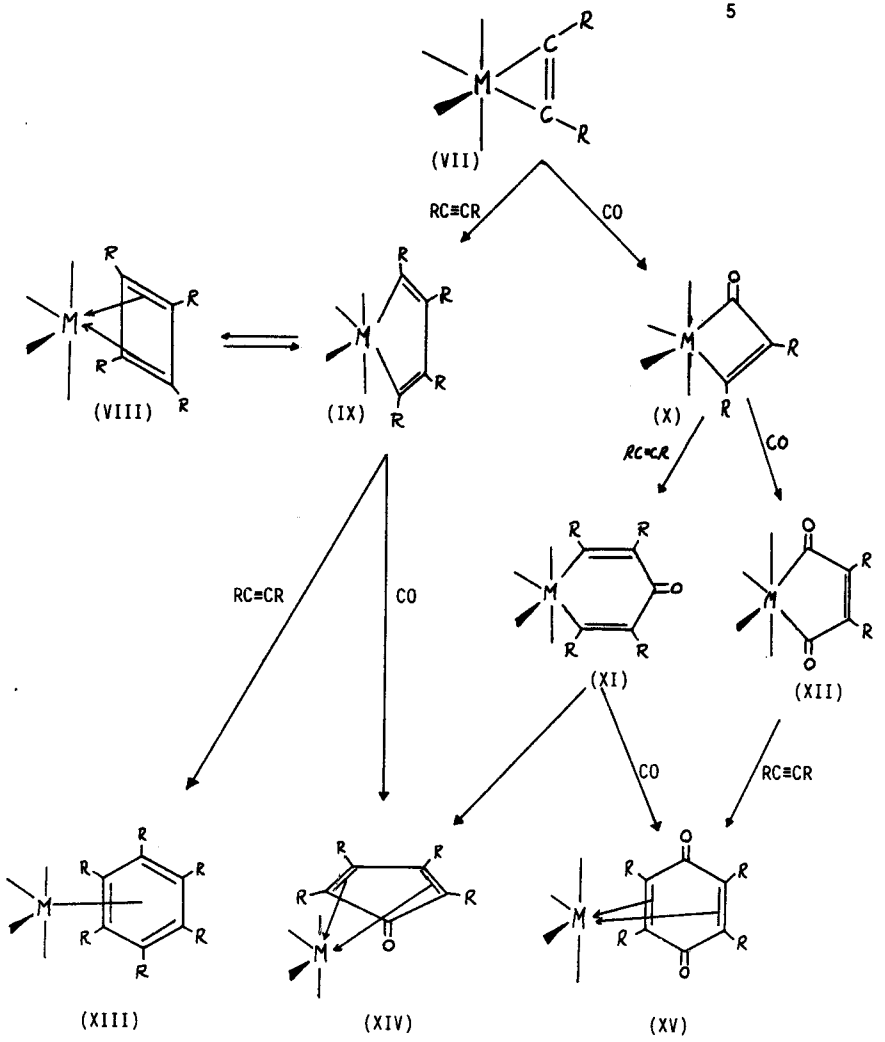
These species are bound to the metal atom through σ or π bonds. Unfortunately, most of the resulting metal-organic complexes are very stable, and the organic products cannot be easily displaced without cleavage inacidic media or via oxidation. An example of this procedure is illustrated in the work of Maruyana and co-workers, where an organometallic compound (V) is treated with ceric ammonium nitrate to give the desired quinone compound (VI).



(V) (VI)

It is therefore to one's advantage in choosing a transition metal which generates few organometallic complexes, while still providing the organizational presence of metal carbonyl species. This property seems inherent in $CpV(CO)_4$, and gives impetus for the characterization of this material as a useful synthetic reagent.

For the most part, the path by which the synthesis of these cyclic organic compounds takes place is still obscure. Once a single acetylenic substrate has added to a monometallic complex, such as for $[(\eta^5\text{-}C_5H_5)V(CO)_2(C_6F_5C{\equiv}CC_6F_5)]$ (4), it becomes clear how such compounds may arise by inspecting the suggested pathways depicted in Scheme I.(15) Depending on the order of acetylenic and/or carbon monoxide addition, different products shall be formed, as directed by the particular

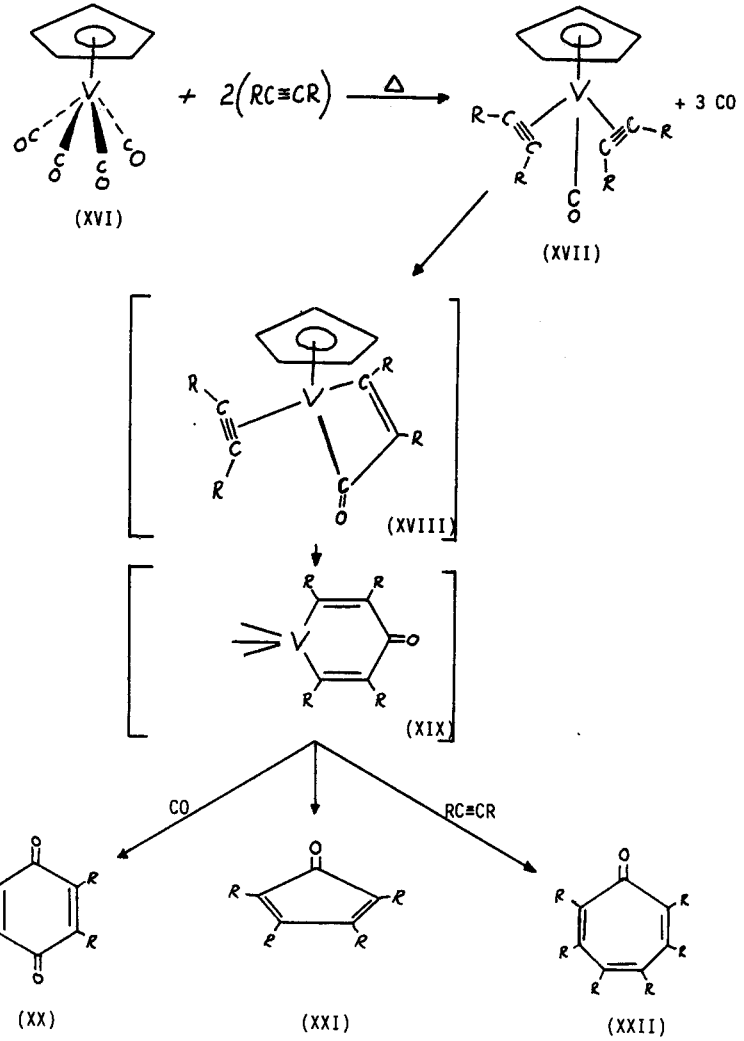


SCHEME I

metal carbonyl complex and the particular acetylene.

Scheme II outlines how three such compounds may be formed, following the loss of the metal as proposed for the vanadium system. Focusing specifically at how $CpV(CO)_4$ might proceed in a similar set of additions, Rausch and Foust have suggested a scheme whereby the vanadium effectively "holds" the acetylenes and carbon monoxide(s) in place until the organic moiety is joined.(4) Sufficiently stabilized, the group detaches itself from the metal as a purely organic product. Their paper also hypothesized that such a reaction mechanism is more likely to proceed if electron-withdrawing substituents (such as $-C_6F_5$) were placed on the acetylenes, as this would help stabilize the complex organometallic intermediates.

It is from such work that this paper shall continue in both experiment and thought. By conducting thermal reactions on a wide variety of substituted acetylenes with $CpV(CO)_4$, where the R groups of RC≡CR may be of electron-withdrawing or donating capabilities, an effort shall be put forth to shed light on the effects of substituent properties in reaction with this carbonyl complex. The primary concern will be the production of cyclic organic compounds, such as the aforementioned cyclopentadeinones, quinones, tropones, and other possible variations. Many organometallic carbonyls have stirred scientific curiosity as possible catalysts, so attention shall also be directed to seek out any possible catalytic activity for this complex of vanadium.



SCHEME II

EXPERIMENTAL

A. Laboratory Techniques

1. General Laboratory Materials and Equipment

All operations were carried out under an argon atmosphere by means of Schlenk techniques. Argon gas was dried by Drierite and 4Å Molecular Sieves.

Pentane, benzene, toluene, methanol, acetonitrile, methylene chloride, diethyl ether, and decalin (decahydronapthalene) were purged of trace oxygen by bubbling argon through the solvents. Benzene was kept free of moisture by storage over metallic sodium. Thionyl chloride was freshly distilled and purged with argon. Spectral grade acetonitrile was freshly distilled and dried over P_2O_5 before use.

Bis(diglyme)sodium hexacarbonylvanadium (-I) was purchased from Strem Chemicals, Inc. η^5-Cyclopentadeinyltetracarbonylvanadium was prepared by a published procedure.(16) Pentafluorophenyl phenyl acetylene, ($C_6F_5C{\equiv}CC_6H_5$) and diferrocenylacetylene were also prepared by published procedures.(17,18)

A prepurified grade argon gas was purchased from Linde Specialty Gases of Union Carbide. Dimethylacetylene dicarboxylate, acetylene dicarboxylic acid, 3-hexyne, bis(trimethylsilyl)acetylene, 2-butyne-1,4-diol, and diphenylacetylene were purchased from the Aldrich Chemical Company. Hexafluoro-2-butyne was obtained from PCR Research Chemicals, Inc.

Anhydrous sodium sulfate and methylene chloride (99 mole % pure) were purchased from the Fisher Scientific Company. Tetramethylsilane and chloroform-d_1 were purchased from Aldrich.

Column chromatography was carried out under argon using either Florisil (60-100 mesh)from Aldrich, or activated and neutral aluminum oxide (60-250 mesh) from Aldrich. Solid samples to be chromatographed were slurried with approximately 2g of the appropriate absorbant and 25ml of diethyl ether. The solvent was removed by vacuum and the coated material applied to the top of a 2.5 x 60cm glass chromatography column packed with the absorbent.

Proton NMR spectra were recorded on a Hatachi Perkin-Elmer R-24A Nuclear Magnetic Resonance Spectrometer and were referenced versus tetramethylsilane (TMS). Infrared spectra were obtained on either a Perkin-Elmer 237 Infrared Spectrophotometer or a Perkin-Elmer 283B Spectrophotometer, using NaCl solution cells or KBr pellets. All IR spectra were referenced versus the 1601.4cm^{-1} absorbtion of polystyrene.

Gas chromatography was performed on a Perkin-Elmer 900 Gas Chromatograph equipped with a Flame Ionization Detector. Mass spectral data were obtained using a Hewlett-Packard 5992 GC/MS System with a 18947A capillary interface and a 5990A GC/MS Vacuum System. Both the GC and the GC/MS systems were equipped with a six-foot, 2% OV101 (mobile phase) on 100-200 W. HP. (stationary phase) nonpolar column and set to flow rates of 25ml/min. Injection temperatures were 300°C. The runs were programmed from 150°-295°C at 15°/min samples having been dissolved in ether.

Fluorescence spectra were recorded on a Perkin-Elmer

Hatachi MPF-2A Spectrophotometer. Ultraviolet-visible spectra were recorded on a Cary 118 Spectrophotometer. Melting points were obtained using a Mel-Temp apparatus from Laboratory Devices, Inc. Melting points are not corrected. High Pressure Liquid Chromatography (HPLC) was performed on a Varian 5000 instrument with Tracor 970A variable wavelength ultraviolet detector.

Unless otherwise noted, thermal reactions of acetylene and $CpV(CO)_4$ were run in a two-to-one mole ratio, using approximately 0.5g of the vanadium complex. A reflux condenser was attached atop a 50ml three-neck round bottom flask fitted with an inlet valve, a magnetic stir bar, and a rubber septum to allow purging with inert gas and solution sampling. The reflux condenser was fitted with an outlet valve, and prior to introduction of the starting materials, the system was purged of it's ambient atmosphere using a vacuum line and argon. Unless otherwise noted, reactions were heated to reflux in toluene and the metal carbonyl absorbtions monitored by infrared analysis. The reaction vessel is depicted in Figure 2.

THERMAL REACTION VESSEL

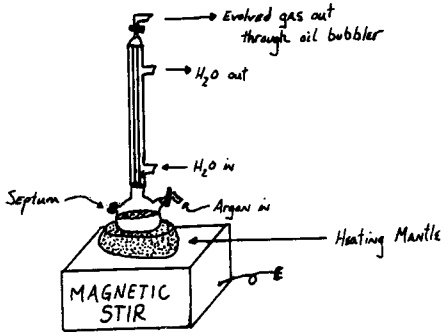


Figure 2

2. Special Techniques

(a) Sealed tube reactions

These reactions were carried out under inert atmosphere using the apparatus depicted in Figure 3. Once a solution of $CpV(CO)_4$ and an acetylene was mixed into toluene and delivered into the tube (using the apparatus in Figure 4), the liquid mixture was frozen in liquid nitrogen and all dissolved gases were removed under vacuum. The tube was flame-sealed, and the closed vessel allowed to warm up to room temperature. Following thermal reaction in an oil bath, the tube was cooled and refrozen to reduce the internal pressure. The vessel was then cracked open, allowed to warm up, and remaining work-up was carried out as previously described.

(b) Sublimations

When purification of solid products was required, sublimations would be carried out in a vessel such as that depicted in Figure 5. The sample would betransferred to a round bottom flask with glass wool above it, attached to a reflux condenser and outlet valve, and submersed in an oil bath. The system would be placed under vacuum, and the product would sublime and recondense on the cooled reflux condenser.

SEALED TUBE REACTION

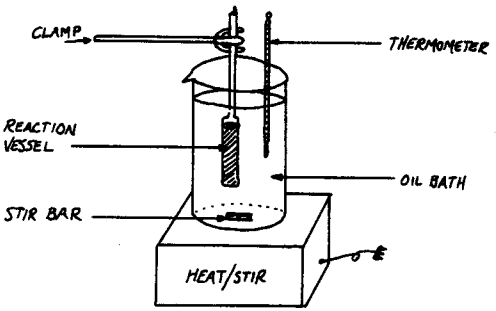


Figure 3

APPARATUS FOR TRANSFERRING MATERIALS UNDER ARGON IN SEALED REACTIONS

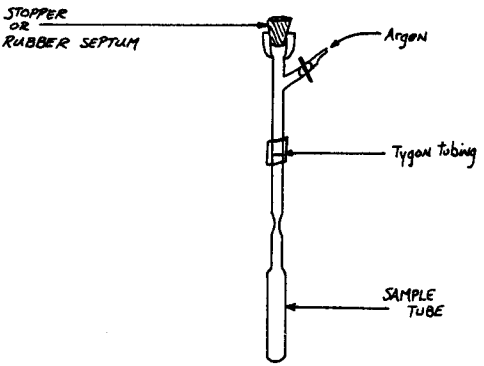


Figure 4

SUBLIMATION APPARATUS

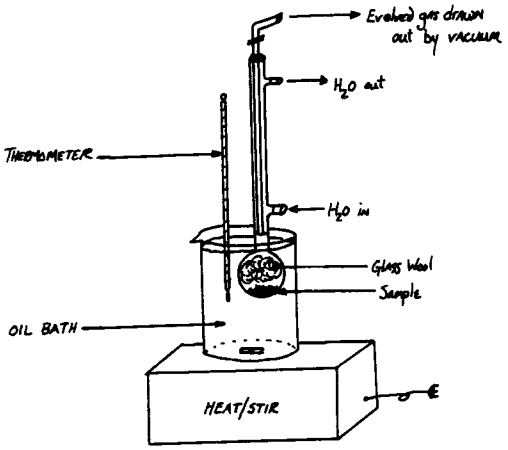


Figure 5

B. Reactions of η^5-Cyclopentadienyltetracarbonylvanadium

1. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and 3-hexyne

An orange solution of 0.50 g (2.2 mmol) of $CpV(CO)_4$ and 0.52ml (4.6 mmol) of 3-hexyne in 40ml of toluene was heated to reflux for 22 hours. Gas was evolved and the solution turned brown. The mixture was cooled and the solvent removed by vacuum. The resulting residue was chromatographed of Florisil. Elution with diethyl ether brought down a yellow band, which was subsequently combined (following infrared spectral comparison of carbonyl absorbtions) with a gold band eluted with a 50% ether/methanol mixture. The sample was extracted from an ether-water mixture and dried over anhydrous sodium sulfate. The remaining dark oil was sublimed at 90°C for 48 hours yielding no carbonyl compounds.

2. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and bis(trimethylsilyl)acetylene

An orange solution of 0.50g (2.2 mmol) of $CpV(CO)_4$ and 1.04ml (4.6 mmol) of bis(trimethylsilyl)acetylene was heated to reflux in 40ml of toluene for 48 hours. Gas was evolved and the solution turned dark brown to black in color. The mixture was cooled and the solvent removed by vacuum. The dark solid was chromatographed on Florisil. A yellow-orange band was eluted with a three:one mixture of ether and benzene. An etheral solution of this band was washed with water and dried over anhydrous sodium sulfate. Sublimation at 90°C for 48 hours yielded no compounds containing a CO functionality.

3. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and 2-butyne-1,4-diol

A solution of 0.49g (2.2 mmol) of $CpV(CO)_4$ and 0.40g (4.5 mmol) of 2-butyne-1,4-diol was heated to reflux in 40ml of toluene for 21 hours. Gas evolved during the reaction, then the solution was cooled and the solvent removed by vacuum. The remaining solid was chromatographed on Florisil. A bright yellow band was eluted with a 1:1 mixture of ether and methanol. An ether solution of this mixture was washed with water and dried over anhydrous sodium sulfate. Sublimation at 160°C for three days left an oily liquid which contained no carbonyl functionality.

4. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and acetylene dicarboxylic acid

An orange-yellow solution og 0.51g (2.2 mmol) of $CpV(CO)_4$ and 0.53g (4.7 mmol) of acetylene dicarboxylic acid in 40ml of toluene was heated to reflux for 18 hours. Gas was evolved and the solution turned to brown. The mixture was cooled and the solvent removed by vacuum. The resulting residue was chromatographed on alumina. Elution with benzene and diethyl ether (50% mixture) produced a yellow band. The solvents were removed by vacuum and the samples were dried over anhydrous sodium sulfate in ether. No carbonyl complexes were isolated from the reaction mixture.

5. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and acetonitrile in toluene (1/100 ratio)

An orange solution of 0.46g (2.0 mmol) of $CpV(CO)_4$ and 13ml (200+ mmol) of spectral grade acetonitrile ($CH_3C{\equiv}N$) was heated to reflux in toluene for five days. The reaction was monitored periodically by infrared spectroscopy, which indicated that none of the starting material, $CpV(CO)_4$, had reacted.

6. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and acetonitrile in decalin (1/100 ratio)

In a similar reaction, an orange solution of 0.48g (2.1 mmol) of $CpV(CO)_4$ and 10ml (190+ mmol) of spectral grade acetonitrile was heated to reflux in decahydronapthalene (decalin, BP= 193°C) for five days. Infrared analysis again indicated that no reaction of the vanadium starting material had occured.

7. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and dimethylacetylene dicarboxylate

An orange-brown solution of 0.50g (2.2 mmol) of $CpV(CO)_4$ and 0.56g (4.6 mmol) of dimethylacetylene dicarboxylate ($CH_3O_2CC{\equiv}CCO_2CH_3$) was heated to reflux in 40ml of toluene for 22 hours. The mixture was cooled and the solvent was removed by vacuum. The resulting solid was chromatographed on alumina. A 3:1 mixture of diethyl ether and methanol eluted a distinct yellow band. Following removal of solvent by vacuum and extraction from water, the mixture was dried over anhydrous sodium sulfate in ether. The slightly yellow solid was sublimed at 150°C and 0.05 mm Hg to give a white crystalline

solid (0.29g, 44.5% yield based on the acetylene as the limiting reagent). Analysis identified the product to be a trimerized acetylene structure, $C_{18}H_{18}O_{12}$, or the hexamethyl ester of Mellitic Acid.

M.P.= 185-187°C (literature M.P.= 187-188°C) (19)

IR (KBr): ν_{CO}= 1737cm^{-1}, ν_{COC}= 1226cm^{-1} See page A-3

NMR (chloroform-d_1): δ3.88ppm (s) See page A-4

GC (ether): single peak at 8.8 minutes

UV/Visible (methanol): λ_{max}= 269nm (= 4.01 x 10^5)

Fluorescence (methanol): λ_{max} at 365nm

Excitation λ = 306nm

Excitation Slit = 7m See page A-5

HPLC (methanol): single peak at 3.35 minutes

Composition of mobile phase:

63% acetonitrile / 27% water

Variable Wavelength Detector @ 269nm

Mass spectrum: m/e = 426 (M+) See page A-6

(literature m/e = 426 (M+)) (20)

8. Thermal reaction of (η^5-C_5H_5)$V(CO)_4$ and dimethylacetylene dicarboxylate in toluene (1/5 ratio)

An orange-brown solution of 0.46g (2.0 mmol) of $CpV(CO)_4$ and 1.24ml (10.1 mmol) of dimethylacetylene dicarboxylate was heated to reflux in 40ml of toluene (BP = 111°C) for 22 hours. Gas evolved, the mixture was cooled and the solvent removed by vacuum. The residue was chromatographed on Florisil. Elution with ether produced a yellow

band. An etheral solution of this mixture was washed with water and dried over sodium sulfate. Sublimation for 48 hours at 140-146°C and 0.03 mm Hg yielded 0.60g (70% based on $CpV(CO)_4$) of the hexamethyl ester of Mellitic Acid ($C_{18}H_{18}O_{12}$).

M.P.= 189-190°C (literature M.P.= 187-188°C) (19)

9. Thermal reaction of (η^5-C_5H_5)$V(CO)_4$ and dimethylacetylene dicarboxylate in xylene (1/5 ratio)

An orange-brown solution of 0.50g (2.2 mmol) of $CpV(CO)_4$ and 1.33ml (10.9 mmol) of dimethylacetylene dicarboxylate was heated to reflux in 40ml of xylene for 5 hours. Gas evolved during the time of reflux, the mixture was cooled and the xylene removed by vacuum. The remaining residue was chromatographed on Florisil. Elution with ether produced an intensely yellow band which yielded a white solid upon evaporation. Sublimation for 60 hours at 150°C and 0.05 mm Hg gave 0.37g (39.7% yield, based on $CpV(CO)_4$) of the hexamethyl ester od Mellitic Acid ($C_{18}H_{18}O_{12}$).

M.P.= 186-188°C (literature M.P.= 187-188°C) (19)

10. Thermal reaction of (η^5-C_5H_5)$V(CO)_4$ and dimethylacetylene dicarboxylate in benzene (1/5 ratio)

An orange-brown solution of 0.50g (2.2 mmol) of $CpV(CO)_4$ and 1.40ml (11.4 mmol) of dimethylacetylene dicarboxylate was heated

to reflux in 40ml of benzene (BP = 80°C) for twelve days. Gas evolved, the solution was cooled and the solvent removed by vacuum. The resulting residue was chromatographed on Florisil. Elution with diethyl ether produced the same yellow band as previously observed, again yielding the hexamethyl ester of Mellitic Acid. Sublimation at 150°C and 0.05 mm Hg gave 0.46g (49.0% based on $CpV(CO)_4$) of the $C_{18}H_{18}O_{12}$ product.

M.P. = 186°C (literature MP = 187-188°C) (19)

The results of reactions 8-10 are summarized in Table 1.

PRODUCT DISTRIBUTION FROM THE THERMAL REACTION OF $(\eta^5\text{-}C_5H_5)V(CO)_4$ AND DIMETHYLACETYLENE DICARBOXYLATE (1:5 RATIO)

SOLVENT	REFLUX TEMP. (°C)	REFLUX TIME (h)	PRODUCT YIELD* ($C_{18}H_{18}O_{12}$)
Benzene	80	288	49.0
Toluene	111	22	70.0
Xylene	138	5	39.7

TABLE 1

*hexamethyl ester of Mellitic Acid, yields based on $CpV(CO)_4$ as the limiting reagent.

11. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and diphenylacetylene

A solution of 0.52g (2.3 mmol) of $CpV(CO)_4$ and 0.87g (4.8 mmol) of diphenylacetylene was heated to reflux in 40ml of toluene for 24 hours. The mixture evolved gas, the solution was cooled and the toluene removed by vacuum. The dark solid was chromatographed on Florisil. Elution with benzene gave a small amount of a yellow solid, which based upon color, infrared analysis, mass spectral data, and elution time appears to be the 2,3,5,6-tetraphenyl-1,4-benzoquinone. (21)

IR (toluene): ν_{CO}= 1653cm^{-1} See page A-7
GC (ether): single peak at 5.8 minutes
Mass spectrum: m/e = 388 (M^+ - 24) See page A-8

Elution with a 50% mixture of benzene and ether produced an intensely purple band, which following solvent removal yielded the major product, 2,3,4,5-tetraphenylcyclopentadienone. (22)

IR (toluene): ν_{CO}'= 1705cm^{-1}

Elution with methanol gave an orange-yellow product which was determined to be the 2,3,4,5,6,7-hexaphenylheptatrienone.

IR (toluene): ν_{CO}= 1685cm^{-1} See page A-9
GC (ether): single peak at 10.9 minutes
Mass spectrum: m/e = 546 (M^+ - oxygen) See page A-10

12. Thermal reaction of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and pentafluorophenyl phenyl acetylene (1/4 ratio)

A solution of 0.38g (1.6 mmol) of $CpV(CO)_4$ and 0.93g (6.2 mmol) of pentafluorophenyl phenyl acetylene, $[(C_6F_5)C{\equiv}C(C_6H_5)]$, was heated to reflux in 40ml of toluene for 26 hours. Gas was evolved, the mixture was subsequently cooled and the solvent removed by vacuum. The dark solid was chromatographed on Florisil, and elution with a 3:1 mixture of benzene and pentane brought down a bright yellow band. This band was washed with water by extraction from ether and dried over anhydrous sodium sulfate. Removal of the solvent by vacuum produced one or both of the isomers of the hexa-substituted benzene; 1,3,5-(tripentafluorophenyl)-2,4,6-(triphenyl)benzene and 1,3,4-(tripentafluorophenyl)-2,5,6-(triphenyl)-benzene.

IR (toluene): ν_{CC} = 1500cm^{-1} and 1650cm^{-1} See page A-11

GC (ether): Two peaks at 9.0 and 11.4 minutes

Mass spectra: m/e = 800 See page A-12

m/e = 790 See page A-13

A 1:1 mixture of benzene and diethyl ether eluted an orange-red band which was washed with water by extraction from ether and dried over anhydrous sodium sulfate. The solvents were removed by vacuum, leaving a mixture of isomers of di(pentafluorophenyl)-diphenylcyclo-pentadienone.

IR (toluene): ν_{CO}= 1700cm^{-1}

GC (ether): Two peaks at 7.9 and 8.4 minutes

Mass spectra: m/e = 564 (M^+) See page A-14

m/e = 580 (M^+ + oxygen) See page A-15

13. **Thermal reaction of (η^5-C_5H_5)V(CO)$_4$ and diferrocenylacetylene**

An orange solution of 0.34g (1.5 mmol) of $CpV(CO)_4$ and 1.25g (3.2 mmol) of diferrocenylacetylene was heated to reflux in 40ml of toluene for 36 hours. Gas evolved during the reaction. The mixture was cooled, the solvent removed by vacuum, and the resulting residue chromatographed on Florisil. Elution with benzene produced an orange band, which was washed with cold pentane and filtered dry to yield 0.040g (1.0 x 10^{-4} mol) of a rust-colored solid, determined to be unreacted diferrocenylacetylene. Analysis by thin layer chromatography confirms this analysis.

M.P. = 238°C (pure diferrocenylacetylene M.P.= 245°C)

IR (toluene): ν_{CO}= 1640cm^{-1} and 1680cm^{-1} See page A-16

UV/Visible (methanol): λ_{max}= 212nm

Compare to spectra of pure diferrocenylacetylene See page A-17

NMR: See page A-18

A red-orange band was eluted with ether, washed with cold pentane and filtered dry. A darker, lower-melting solid (M.R.= 120-130°C) was obtained (0.029g). This was an impure carbonyl compound, contaminated in part with unreacted diferrocenylacetylene. Spectral

and physical analyses were inconclusive as to the compound's identity.

IR (toluene): ν_{CO}= 1650cm^{-1} and 1680cm^{-1} See page A-19

NMR: See page A-20

14. Thermal reaction of (η^5-C_5H_5)$V(CO)_4$ and hexafluoro-2-butyne (1/25 ratio)

A dark red-brown solution of 0.62g (2.7 mmol) of $CpV(CO)_4$ and 12.5g (77.2 mmol) of hexafluoro-2-butyne was heated to 111°C in approximately 40ml of toluene for five days in a sealed tube. The mixture turned to dark brown. The solution was cooled, and once the excess acetylene boiled off ($CF_3C{\equiv}CCF_3$, BP = -24.6°C), the solvent was removed by vacuum. The brown solid was chromatographed on Florisil. Elution with ether brought out a dark band, which yielded 0.47g of dark metallic crystals. Although a comparison of physical properties to published results discounts a number of possible structures, no structure may be positively confirmed. (23-25)

M.P. = above 330°C, no decomposition to 330°C.

IR (KBr): ν_{CO}=1600cm^{-1} and 1730cm^{-1} See page A-21

UV/Visible (CH_2Cl_2): λ_{max}= 239nm See page A-22

C. Reactions of Bis(diglyme)sodium hexacarbonylvanadium (-I)

1. Thermal reaction of $Na(C_6H_{14}O_3)_2V(CO)_6$ and dimethylacetylene dicarboxylate

A solution of 1.00g (2.0 mmol) of $Na(C_6H_{14}O_3)_2V(CO)_6$ and 0.58g (4.1 mmol) of dimethylacetylene dicarboxylate was heated to reflux in 40ml of toluene for 48 hours. The solution was cooled, the solvent removed by vacuum, and the residue chromatographed on Florisil. A 2:1 mixture of benzene and diethyl ether eluted a dark yellow band, which following sublimation at 150°C and 0.05 mm Hg for 48 hours produced no carbonyl compounds.

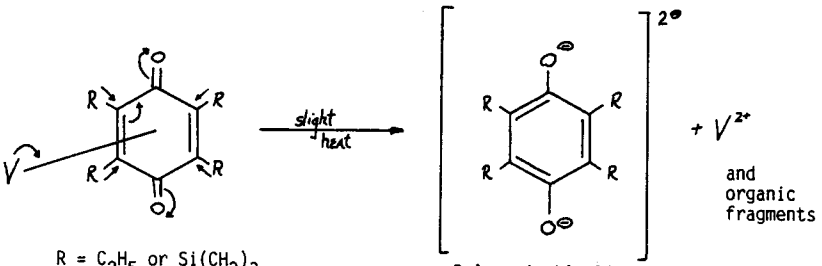
RESULTS AND DISCUSSION

A. Reactions of η^5-Cyclopentadienyltetracarbonylvanadium

No carbonyl compounds were isolated as products from the reaction of 3-hexyne ($C_2H_5C{\equiv}CC_2H_5$) and $CpV(CO)_4$, even though all of the vanadium carbonyl compound was consumed during the process (as inferred by the absence of metal carbonyl stretches in the infrared between $2200cm^{-1}$ and $1850cm^{-1}$ - See page A-1). It is possible that an organic product not containing a carbonyl functionality may have formed, however investigation in this area was not pursued. The acetylene, having an electron-donating ethyl substituent, may simply not have been able to stabilize the intermediate complex (compound XVIII), thus precluding the possibility of any organic carbonyl compound being produced.

A similar situation occurred in the reaction of bis(trimethylsilyl)acetylene [$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$] with $CpV(CO)_4$, as again no organic carbonyl complexes were isolated. Infrared analysis indicated that $CpV(CO)_4$ was completely consumed. Just as electron-donating as $-C_2H_5$, the $-Si(CH_3)_3$ substituted acetylene must not stabilize intermediate XVIII. Perhaps the overwhelming presence of four donating groups on even a fleeting p-benzoquinone derivative would cause these compounds to either polymerize of decompose (while still coordinated to the metal) to some simpler organic structure, as suggested in Reaction I.

Of course, this explanation is only suggested for the



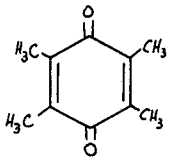
R = C_2H_5 or $Si(CH_3)_3$

Polymerizable Dianion

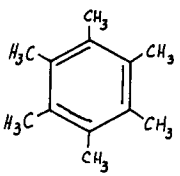
REACTION I

vanadium system, as similar quinone derivatives have been formed using other transition metal carbonyl compounds in such a fashion. (It should be noted that in every reaction run throughout this study of $CpV(CO)_4$, an intractable material was consistently chromatographed with methanol or water - a vanadium salt of some sort. At this time, no analysis has been conducted to see what form the vanadium finally assumes. This ought to be further pursued.) Isolation of other possible products was not carried out in these cases.

Duroquinone, or 2,3,5,6-tetramethyl-p-benzoquinine (compound XXIII), and hexamethylbenzene (compound XXIV) have been formed in a related reaction between 2-butyne ($CH_3C{\equiv}CCH_3$) and bis(chlorodicarbonyl-rhodium), $[Rh(CO)_2Cl]_2$. (26)

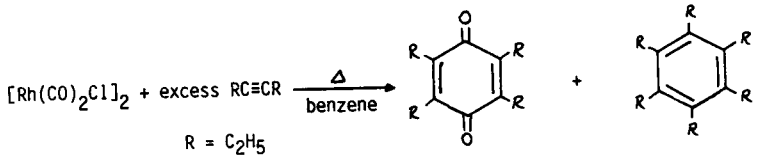


(XXIII)



(XXIV)

This paper also reported the reaction of $[Rh(CO)_2Cl]_2$ with 3-hexyne, in which the desired (and expected) products were obtained. These results are summarized in Reaction II.



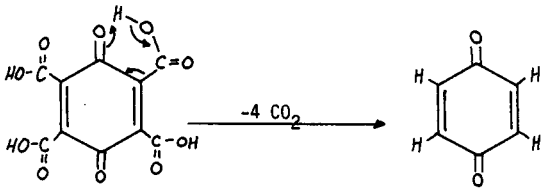
REACTION II

Such a comparison verifies that even though a particular transformation of matter may be carried out in the presence of one particular metal carbonyl compound, in this case a Group VIII metal, comparable results are not always the case when using a metal from Group VB. This vanadium system is unique, and therefore results cannot necessarily be predicted.

Of slightly less donating ability are the $-CH_2OH$ groups on 2-butyne-1,4-diol ($HOCH_2C{\equiv}CCH_2OH$). The reaction of this acetylene with $CpV(CO)_4$ yielded a small amount of a carbonyl-containing compound (according to infrared analysis), however this material was not isolated.

The reaction between $CpV(CO)_4$ and acetylene dicarboxylic acid ($HOOCC{\equiv}CCOOH$) yielded no organic carbonyl complexes, and definitely not the tetracarboxylic acid quinone derivative, as this unknown compound (XXV), a β- keto acid, would spontaneously lose up to four equivalents

of carbon dioxide (CO_2), as outlined in Reaction III.

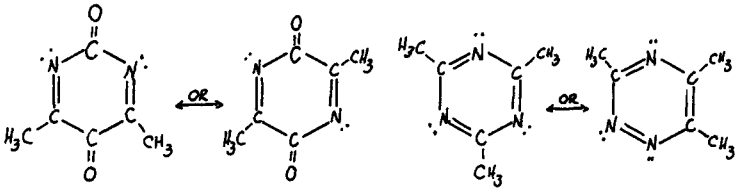


(XXV) (XXVI)

REACTION III

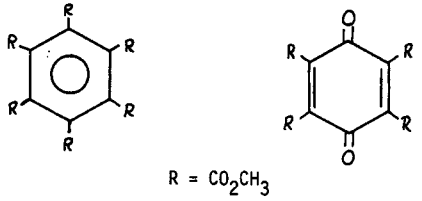
Decarboxylation of an acid will occur most readily if, within group R- for a general acid RCOOH, there is a strongly electron-attracting substituent such as $-NO_2$ or C=O. (27) In this case, the ketone functionality is to the acid group, so that if compound (XXV) ever did form, it would immediately decompose to compound (XXVI). Spectral analysis shows, however, that no quinone was formed whatsoever, so neither compounds (XXV) or (XXVI) ever existed in this process.

An attempt to generate heterocyclic organic carbonyl complexes was the basis for the reactions of $CpV(CO)_4$ with acetonitrile ($CH_3C{\equiv}N$) in both toluene (BP= 111°C) and decalin (decahydronapthalene, BP= 193°C). Using the acetonitrile not as an acetylene, but as a source of a triple bond, these two reactions were run to see if the vanadium complex would aid the production of hypothetical (XXIIa & b),or catalyze the trimerization of acetonitrile to form compounds (XXIIIa & b). Although creative in thought, infrared analysis indicated that the $CpV(CO)_4$ did not react under either condition.



(XXVIIa) (XXVIIb) (XXIIIa) (XXVIIIb)

The thermal reaction of $CpV(CO)_4$ with two equivalents of dimethylacetylene dicarboxylate ($CH_3O_2CC{\equiv}CCO_2CH_3$) produced the trimerized product (XXIX), the hexamethyl ester of Mellitic Acid, instead of the "expected" and as yet unknown compound (XXX).



R = CO_2CH_3

(XXIX) (XXX)

This was determined using a number of methods. The melting point of 188-189°C is consistent with the literature, as is the product's white crystalline form. (28) The infrared spectrum for this compound (See A-3) shows a strong $-\overset{O}{\overset{\|}{C}}-$ absorbtion at $1737cm^{-1}$ and a characteristic C-O-C absorbtion at $1226cm^{-1}$. This may be compared to the $2200cm^{-1}$ - $1800cm^{-1}$ region of both the pure $CpV(CO)_4$ (See page A-1) and the pure dimethylacetylene dicarboxylate (See page A-2) to verify that all of

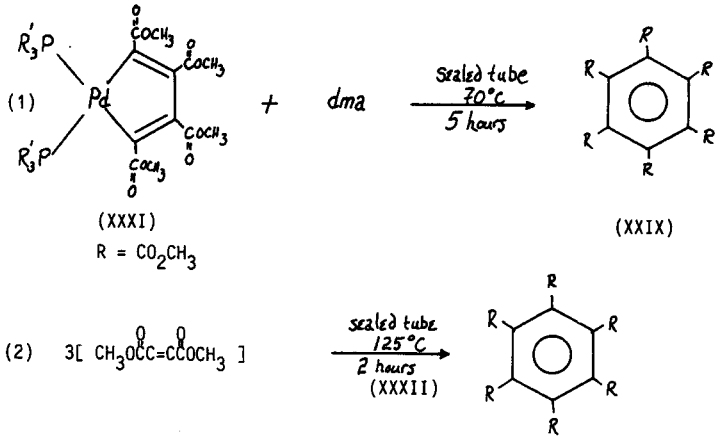
the starting materials were consumed. The NMR spectrum (See page A-4) shows a singlet at 3.88 ppm, and the UV/Visible analysis gives $_{max}$ in ethanol at 269nm. Excitation at 306nm gives a broad fluorescence maximum at 365nm. The compound readily sublimes and is air-stable.

Since compound (XXIX) was generated in nearly 45% yield, subsequent reactions were run in an effort to optimize reaction conditions. The same reaction was rerun, however increasing the acetylene-to-$CpV(CO)_4$ ratio from two-to-one to five-to-one. This had a profound effect on the reaction's efficiency, as 70% of the theoretically obtainable material was recovered. Encouraged by these results, the 5:1 ratio was repeated, however instead of using toluene (BP = 111°C) as the solvent, p-xylene (BP = 138°C) was used. Although the yield fell from 70.0% to 39.7%, the reaction time was less than 25% of the time required in the lower boiling solvent (See Table 1). If the time factor is an important consideration to the chemist, the more rigorous conditions may be desired, as a fourty percent yield is still quite acceptable.

Carrying this process one step further, the same five-to-one ratio of acetylene to $CpV(CO)_4$ was set up in a reaction with benzene (BP = 80°C) as the solvent. Time becomes a major consideration here, as twelve days were required to obtain a 49.0% yield of the hexamethyl ester of Mellitic Acid. The $(\eta^5\text{-}C_5H_5)V(CO)_4$ was not fully consumed, indicating that either the reaction conditions were simply not optimized, or that the $CpV(CO)_4$ is acting as a catalyst at this lower temperature. This may be the better explanation, as infrared analysis indicates that the vanadium carbonyl compound was largely unreacted, though still generating the benzene derivative in good yield.

The most encouraging results came from the reaction in toluene, as the time required was reasonable, and the yield was high. It seems that at this temperature the reaction may efficiently proceed while still allowing the Mellitic Acid derivative to remain intact. The higher temperatures must be too vigorous, breaking up some of the desired product and reducing yield.

A fair amount of research has been conducted on the trimerization of dimethylacetylene decarboxylate (dma). An early paper by Otto Diels carried out the procedure in the presence of pyridine - the base acting as a sort of "enzyme", holding the acetylene fragments in place until the benzene derivative could be joined. (28) Since that time, more elegant studies have been conducted on the catalytic trimerization of dma in the presence of various transition metals, including rhodium, palladium, cobalt and molybdenum. (29-32) Two examples of these trimerizations are illustrated in Scheme III.

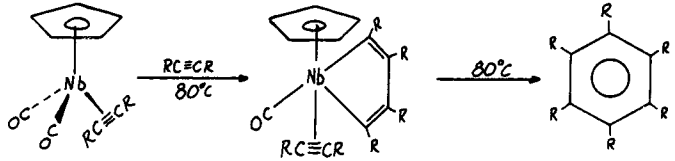


SCHEME III

In the first reaction, the catalyst $\{[P(C_6H_5)_3]_2Pd(C_2R_4)\}$, R = CO_2CH_3 compound (XXXI), promotes the reaction of dma to form sixty equivalents of the benzene derivative per equivalent of catalyst (64% based on dma). The second reaction illustrates the catalysis of dimethylacetylene dicarboxylate in the presence of $[Pd_2(dpm)_2Cl_2]$, [compound(XXXII),dpm= bis(diphenylphosphino)methane], to yield 40% of the hexamethyl mellitate.

Compared to these systems, this work with $CpV(CO)_4$ as a catalyst is very promising, as it is the first vanadium complex found to trimerize dma to date, and with great efficiency. It requires one equivalent of the $CpV(CO)_4$ for every three equivalents of acetylene, and it was on this premise that the yield determinations were made.

An analogous study has been conducted on a cogener of vanadium. η^5-Cyclopentadienlydicarbonylniobium diphenylacetylene, $[(C_5H_5)Nb(CO)_2Ph_2C_2]$, compound (XXXIII), was used in an attempt to catalytically trimerize diphenylacetylene. (33) This work discovered, however, that the niobium complex did not catalyze the trimerization, but that the hexaphenylbenzene (compound XXXIV) resulted from the stoichiometric, thermal breakdown of compound (XXXIII) in Reaction IV.



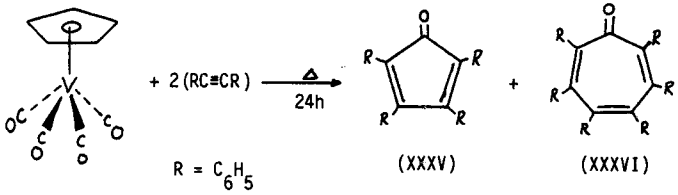
(XXXIII) (XXXIV) (XXXV)

R = C_6H_5

REACTION IV

Such an explanation may be valid for our vanadium analog, however no data supports this suggestion. The conditions used in this case were more vigorous, and the acetylenic substituent ($-CO_2CH_3$) is quite different in both bulkiness and electron-withdrawing ability from a phenyl group. A closer investigation into the actual mechanism of this reaction is in order, to support or refute this claim of possible catalysis; however it must be left for future researchers. The results of this process have thus been reported.

The reaction of $CpV(CO)_4$ and diphenylacetylene produced at least two distinguishable cyclic organic carbonyl compounds, and possibly a third as well. Reaction V outlines the results.



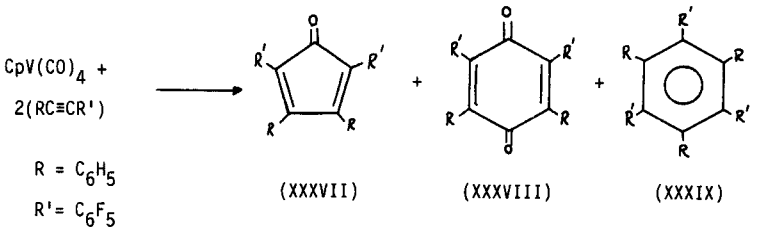
REACTION V

Compound (XXXV), the 2,3,4,5-tetraphenylcyclopentadienone, was obtained as a purple solid with a carbon-oxygen double bond stretch at $1700cm^{-1}$ in the infrared. These results compare well with published results on the compound. (21) The cyclopentadienone clearly represented the largest percentage of products obtained. Compound (XXXVI), or the 2,3,4,5,6,7-hexaphenylcycloheptatrienone, was the other major product obtained. This orange-yellow solid was eluted

from the chromatography column with a more polar solvent than the cyclopentadienone required. Other data are all consistent with results published in an earlier paper. (4)

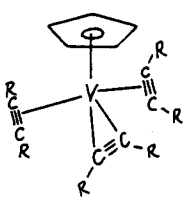
Although the analyses carried out on the possible third product from this reaction show no discounting evidence, undeniable evidence for 2,3,5,6-tetraphenyl-1,4-benzoquinone simply did not present itself in this case. It is probable that this quinone derivative was formed, however further effort in this area was not carried out.

The interesting results occurred when $CpV(CO)_4$ was allowed to react with pentafluorophenyl phenyl acetylene. As the only non-symmetrically substituted acetylene used thus far, it is the first to give a number of isomeric products. Also, it appears that the substitution of a perfluorinated phenyl group for a $-C_6H_5$ group (as in the previous experiment) has a great effect on the outcome of the reaction. Run under analogous conditions for nearly equal lengths of time, the added electron-withdrawing ability of a single perfluorinated ring on the acetylene generated two distinguishable carbonyl complexes (and their isomers), as well as isomers of the trimerized product. These results are outlined generally in Reaction VI.

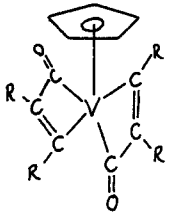


REACTION VI

Unlike reaction eleven, where diphenylacetylene was used to generate primarily the cyclopentadienone and some cycloheptatrienone, reaction twelve (where one of the acetylenic substituents is $-C_6F_5$) clearly produced the benzene derivative, a quinone, and (similarly) a five-membered ring ketone. Strongly electron-withdrawing, the perfluorinated ring must withdraw enough electron density from the metal to allow the organization of either the benzene derivative or the quinone from an intermediate such as compounds (XL) or (XLI).



(XL)



(XLI)

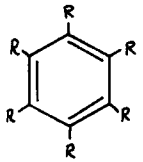
The phenyl groups simply cannot stabilize the intermediates in such a fashion, leaving the metal sufficiently rich in electrons so as not to require additional ligand coordination. It seems logical that the withdrawing ability of any substituents coordinated to vanadium will help to increase the metal's oxidation state, thereby allowing (or perhaps requiring that) additional groups (such as a carbonyl ligand or an acetylene) be brought into the "coordination shell" of the transition metal. In this fashion, one may rationalize the added benefit of using acetylenes appropriately substituted with electron withdrawing groups to produce cyclic organic carbonyl

compounds.

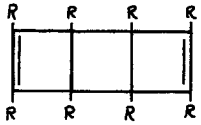
The reaction of $CpV(CO)_4$ and diferrocenylacetylene yielded a fair amount of unreacted acetylene, both in a relatively pure form and as an impurity in other species. Spectral analyses verify the presence of a carbonyl compound, though the results were inconclusive. The major drawback in the analysis was the limitation of the mass spectrometer to only pick out mass units of 800amu or less. If the quinone derivative had formed, it's molecular weight would be 844g/mol. The 2,3,4,5-tetraferrocenylcyclopentadienone would have a molecular weight of 826 g/mol. It is quite probable that some such compound has formed (it has the characteristic infrared ν_{CO}= 1680cm^{-1} and a melting point of 120°C), however the analysis must remain incomplete. The large functional groups have great potential to withdraw electron density from the proposed organometallic intermediate (compound XLI), and this particular reaction would be a facinating study for future work.

The reaction of $CpV(CO)_4$ and the gaseous acetylene hexafluoro-2-butyne represents another instance where a carbonyl compound was probably formed, but analyses fall short of structure verification. The product obtained exhibits a strong absorbtion in the 1500cm^{-1} - 2000cm^{-1} region of the infrared spectrum, indicating that some sort of C-O linkage is present. The extremely high melting point (somewhere above 330°C) suggests that perhaps the compound is polymeric in nature, as few organic structures melt above such a temperature. Compounds (XLII) - (XLIV) may be ruled out on the basis of color and melting point (23-25), and one may infer that the quinone derivative and the tropone derivative are also unlikely. The metallic appearance

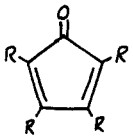
$R = CF_3$



(XLII)



(XLIII)

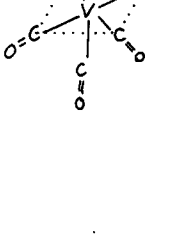


(XLIV)

and high resistance to heat posessed by these crystals leads one to ponder on the possibility of an electrically conductive material, as it has recently been documented that certain acetylenes will polymerize to yield compounds quite similar in appearance and conductivity to metals. (34) If such a process has transpired here, further classification of this material could prove most beneficial.

B. Reactions of Bis(diglyme)sodiumhexacarbonylvanadium (-I)

The only reaction carried out on an acetylene by a species other than $CpV(CO)_4$ was performed using dimethylacetylene dicarboxylate and bis(diglyme)sodium-hexacarbonylvanadium. This experiment was conducted to see if the absence of the cyclopentadienyl ring on the metal would have a significant effect on the trimerization of this reactive acetylene. As outlined in Reaction VII, no carbonyl compounds were formed.



$$+ 2(\ CH_3OCC{\equiv}CCOCH_3\ ) \xrightarrow{48h} \text{No Products}$$

REACTION VII

This lack of reactivity may be explaned in two manners. First, the cyclopentadienyl ligand is a stable "cloud" of electron density coordinated to vanadium in $CpV(CO)_4$, and the absence of such a group should prove critical. The metal may now be forced into a higher, and less desirable, oxidation state. Second, compound (XLV) is symmetrically substituted, thus making the loss of a first and second carbon monoxide ligand (as would be

required to effectively "hold" onto reactive alkynes) thermodynamically unfavorable, thereby reducing reactivity. In this situation, the reactants simply decomposed.

SUMMARY

This work is just the "tip of the iceberg." Not only are there a great number of acetylenes left untested at this point, but as referred to in the text, there exist a dozen or so interesting facets to this project which could develop nicely into further work. It now seems apparent that the substituents on the acetylenes are critical parameters in reactions of $CpV(CO)_4$. The more electron-withdrawing power one places on an acetylene, the more likely you are to generate cyclic organic products.

As with many transition metal carbonyl complexes, η^5-cyclopentadienyltetracarbonylvanadium shows both "enzymatic" and catalytic properties, as dependent upon particular reaction conditions and reagents. Effort in this area would be of interest to students of the lesser known transition elements (we are all students), as isolated reaction intermediates could shed light on the noted organizational abilities and requirements of $(\eta^5\text{-}C_5H_5)V(CO)_4$.

This thesis represents but a small step in the characterization of this vanadium complex. Serious effort should be exerted in this and related areas, to further unleash the true potential such materials have

as organic reagents. We have only begun to recognize the possibilities, and further advances will come only to the curious and imaginative soul. Organometallic chemistry is still a young field, largely unknown to many chemists. Use it for the valuable secrets it contains. We all will benefit from such efforts.

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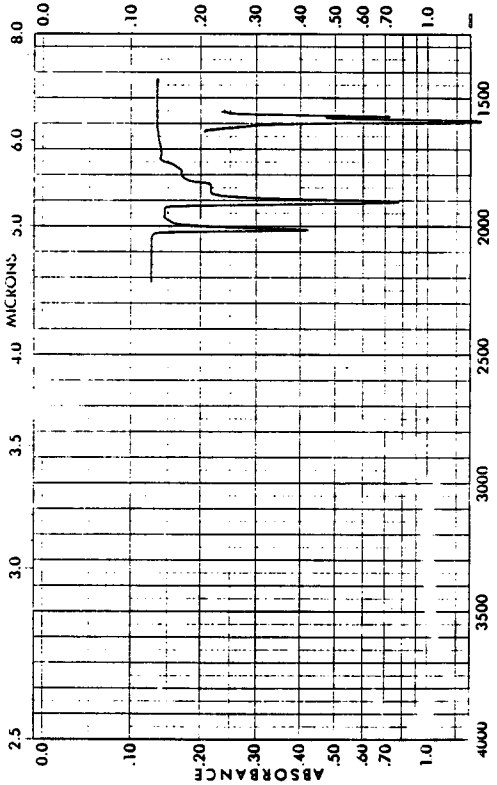
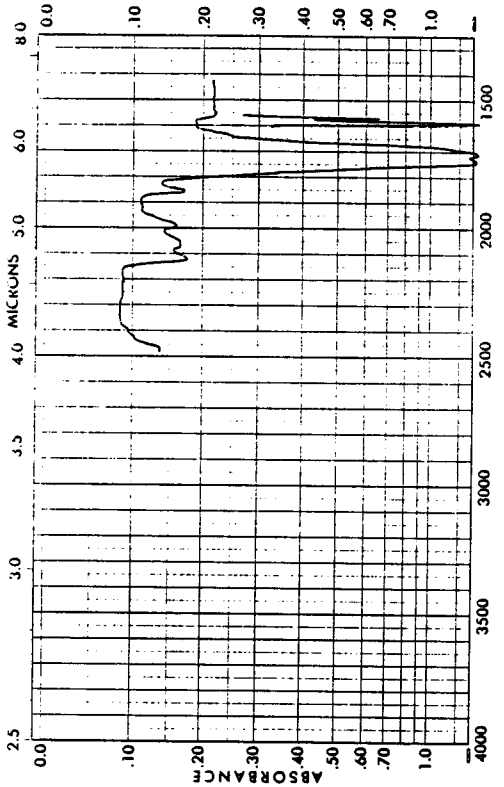
APPENDICES

A-1

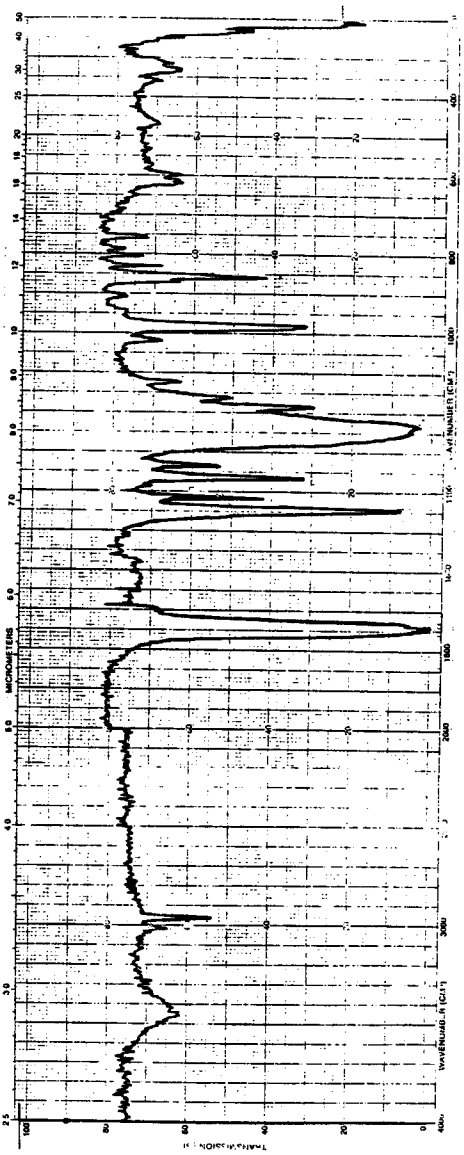
Infrared spectrum of pure $CpV(CO)_4$



Infrared spectrum of dimethylacetylene dicarboxylate

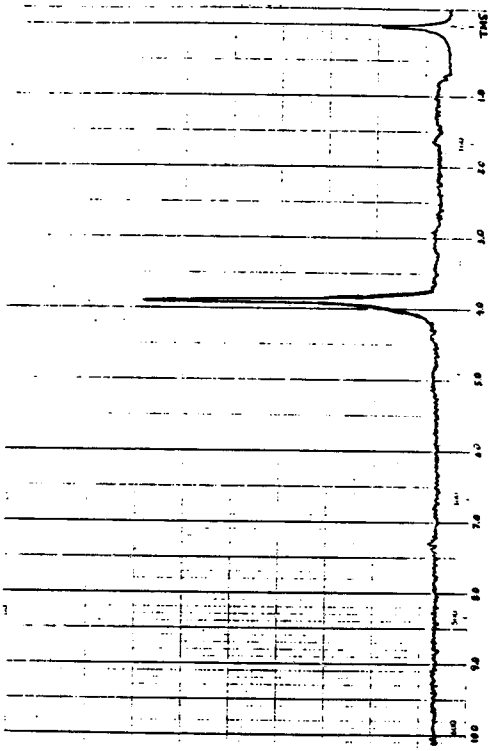


A-3 IR of the hexamethyl ester of Mellitic Acid

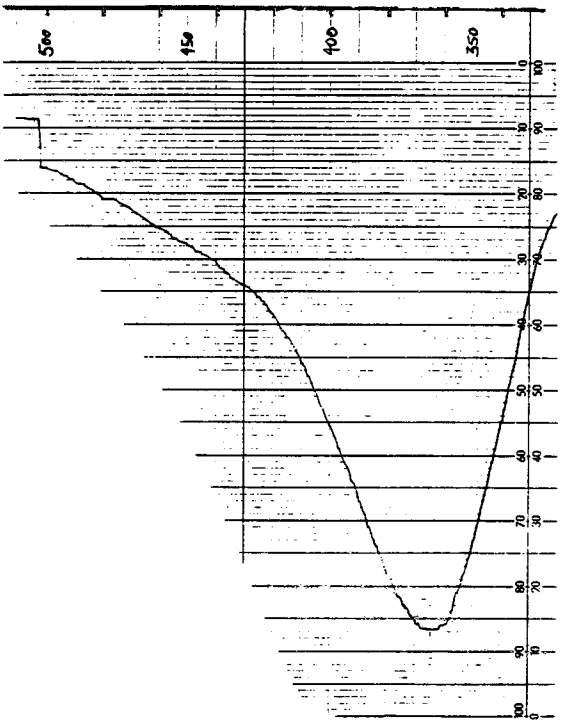


A-4

NMR spectrum of the hexamethyl ester of Mellitic Acid



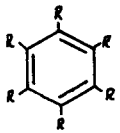
Fluorescence spectrum of the Mellitic Acid derivative



A-6

$C_{18}H_{18}O_{12}$

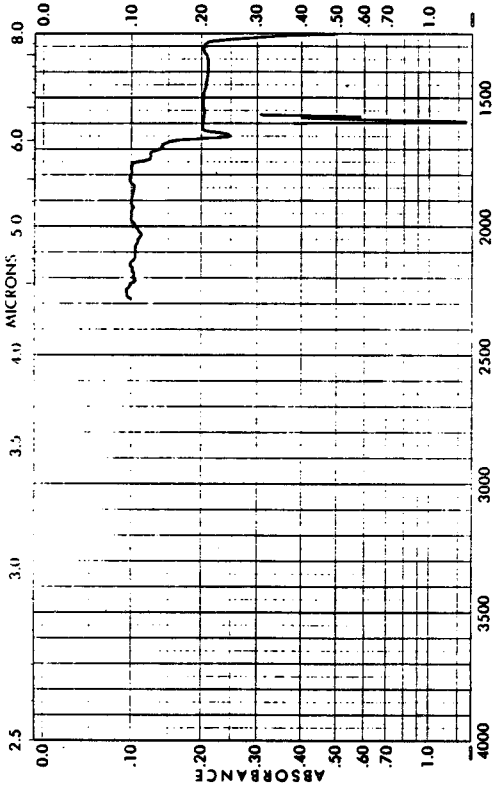
MW = 426g/mol



R = CO_2CH_3

m/e	Relative Intensity	Assignment
426	2.4	M^+
396	20.0	$M^+ - CH_2O$
395	100.0	$M^+ - CH_3O$
364	4.0	$M^+ - 2\ CH_3O$
349	6.8	$M^+ - 2\ CH_3O, CH_3$
220	6.0	$C_{11}H_8O_5^+$
162	14.3	$C_9H_6O_3^+$
104	15.7	
75	9.1	$C_2H_3O_3^+$

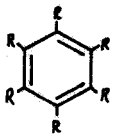
Infrared spectrum of 2,3,5,6-tetraphenyl-1,4-benzoquinone



A-8

$C_{30}H_{20}O_2$

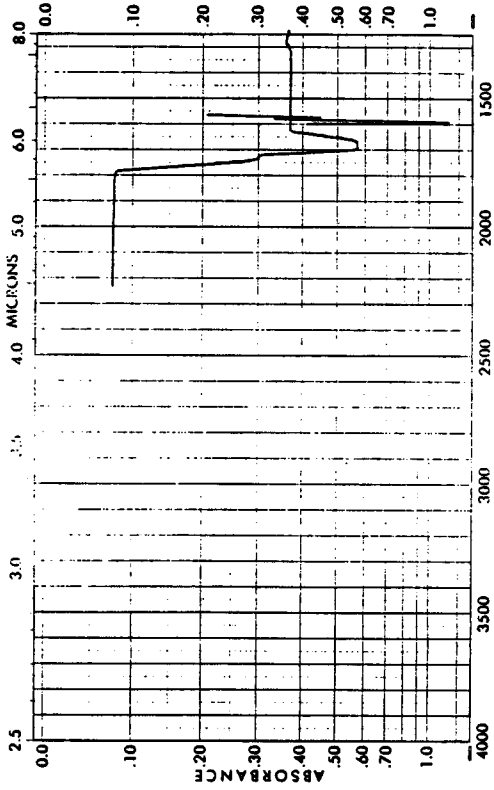
MW = 412g/mol



R = C_6H_5

m/e	Relative Intensity	Assignment
388	5.6	M^+ - 2C
372	27.6	M^+ - CO, C
267	12.9	M^+ - CO, C, C_7H_5O
178	4.6	$C_6H_5C{\equiv}CC_6H_5^+$
105	100.0	$C_7H_5O^+$

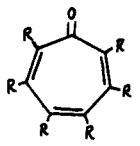
IR of 2,3,4,5,6,7-hexaphenylcycloheptatri none



A-10

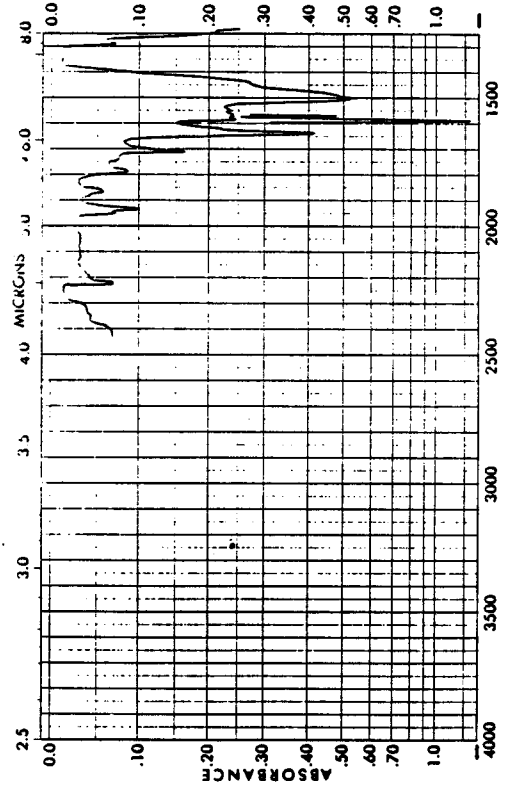
$C_{43}H_{30}O$

MW = 562g/mol



m/e	Relative Intensity	Assignment
546	1.4	M^+ - oxygen
387	12.3	
386	37.4	
385	26.7	
384	86.8	$M^+ - C_6H_5C{\equiv}CC_6H_5$
356	32.5	$C_{28}H_{20}$
307	6.8	$C_{22}H_{15}^+$
299	36.4	
276	10.3	
179	28.4	
178	100.0	$C_6H_5C{\equiv}CC_6H_5^+$
176	19.3	
165	10.5	
152	14.8	

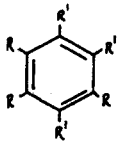
Infrared spectrum of 1,3,5-(tripentafluorophenyl)-
2,4,6-(triphenyl)benzene



A-12

$C_{42}F_{15}H_{15}$

MW = 804 g/mol



Retention time = 9.2 minutes

R = C_6H_5

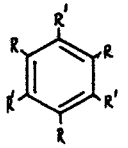
R'= C_6F_5

m/e	Relative Intensity	Assignment
790	11.2	
789	26.8	
639	43.1	$M^+ - C_6F_5 + 2$
638	100.0	$M^+ - C_6H_5 + 1$
573	2.8	$M^+ - 3(C_6H_5)$
470	9.2	$M^+ - 2(C_6F_5)$

A-13

$C_{42}F_{15}H_{15}$

MW = 804g/mol



Retention time = 11.4 minutes

R = C_6H_5

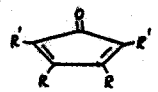
R'= C_6F_5

m/e	Relative Intensity	Assignment
800	10.6	
796	65.7	
470	9.7	$M^+ - 2(C_6F_5)$
268	28.2	$C_6F_5C{\equiv}CC_6H_5^+$
167	9.5	$C_6F_5^+$
77	100.0	$C_6H_5^+$

A-14

$C_{29}F_{10}H_{10}O$

MW = 564g/mol



Retention time = 7.9 minutes

R = C_6H_5

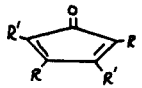
R' = C_6F_5

m/e	Relative Intensity	Assignment
564	56.0	M^+
536	20.1	$M^+ - CO$
459	2.9	$M^+ - CO, C_6H_5$
397	3.8	$M^+ - C_6F_5$
369	7.3	$M^+ - CO, C_6F_5$
269	15.4	
268	100.0	$C_6F_5C{\equiv}CC_6H_5^+$
178	19.6	$C_{14}H_{10}^+$
167	1.6	$C_6F_5^+$
105	5.1	$C_7H_5O^+$
77	9.8	$C_6H_5^+$

A-15

$C_{29}F_{10}H_{10}O$

MW = 564g/mol



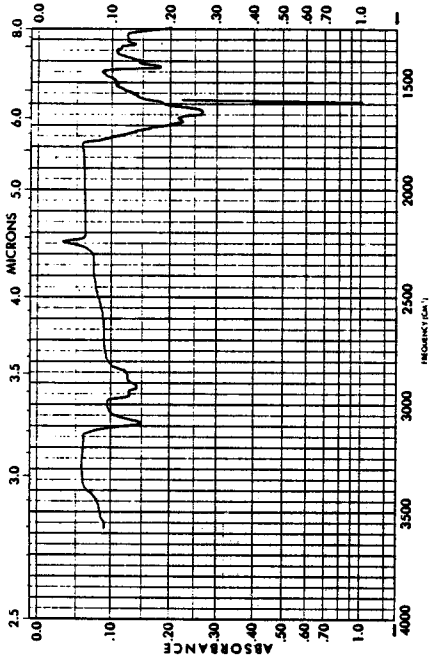
Retention time = 8.4 minutes

R = C_6H_5

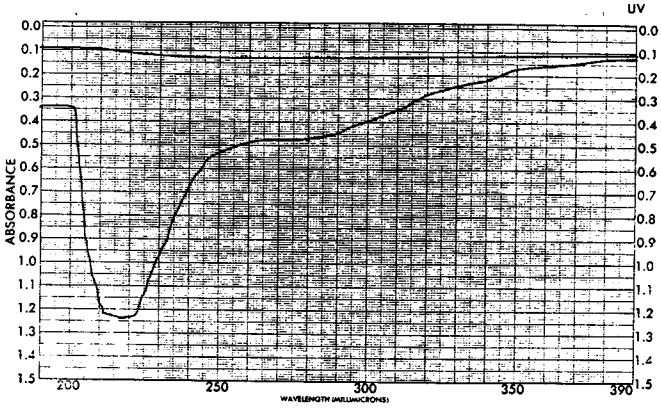
R' = C_6F_5

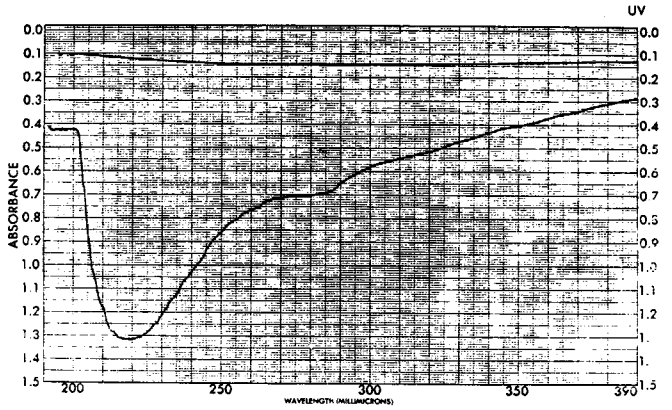
m/e	Relative Intensity	Assignment
580	11.8	M^+ + oxygen
566	7.8	M^+ + 2
565	32.0	M^+ + 1
564	100.0	M^+
552	23.0	M^+ - C
536	28.6	M^+ - CO
459	3.3	M^+ - CO, C_6H_5
397	14.4	M^+ - C_6F_5
369	13.3	M^+ - CO, C_6F_5
269	16.3	
268	51.2	$C_6F_5C{\equiv}CC_6H_5^+$
178	20.2	$C_{14}H_{10}^+$
105	5.4	$C_7H_5O^+$
77	9.0	$C_6H_5^+$

Infrared spectrum of impure diferrocenylacetylene

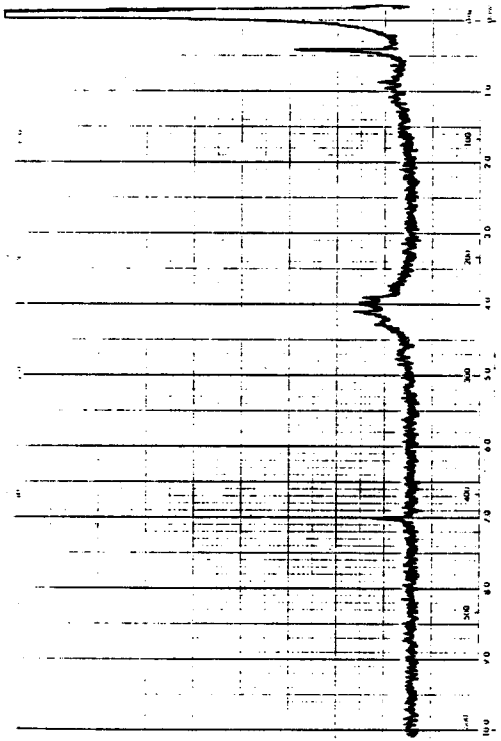


UV/Visible spectral comparison of pure and recovered diferrocenylacetylene



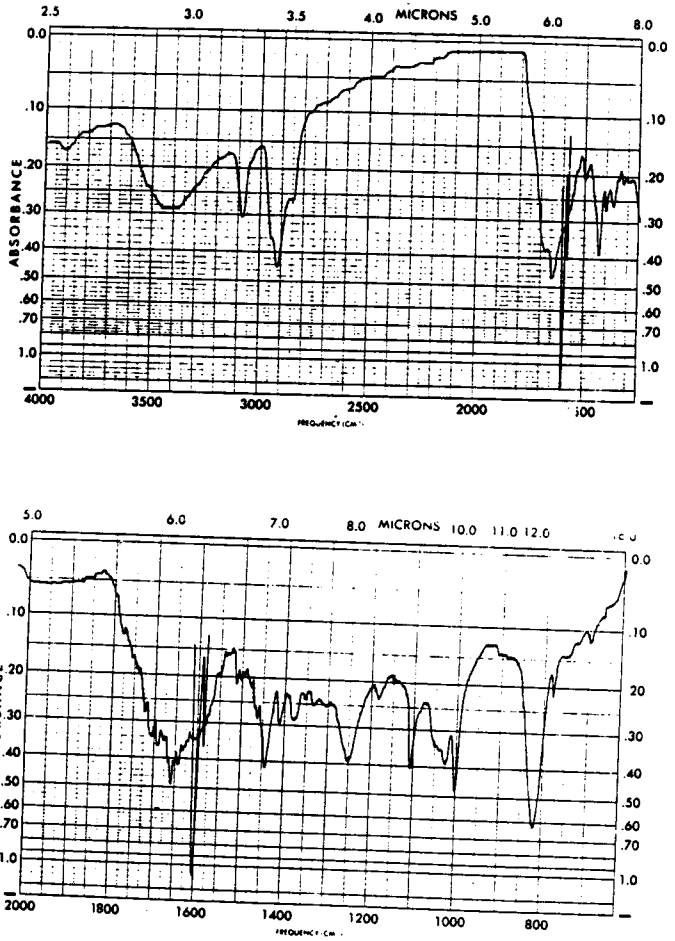


NMR spectrum of impure diferrocenylacetylene

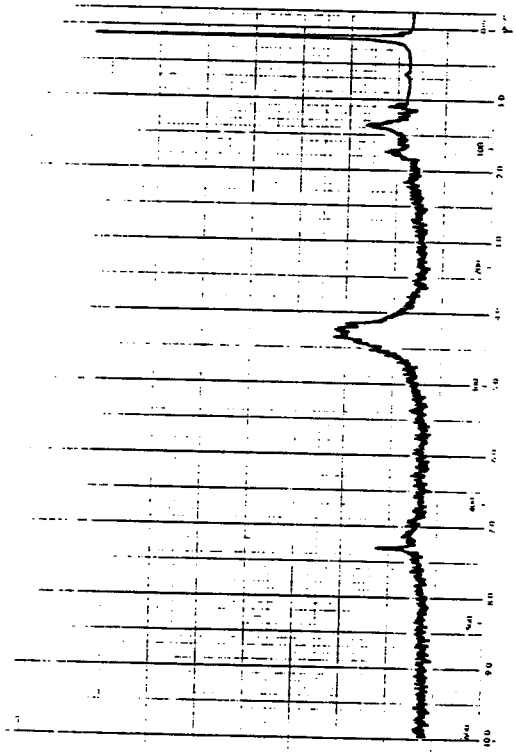


A-19

Infrared spectrum of an unknown compound, reaction 13

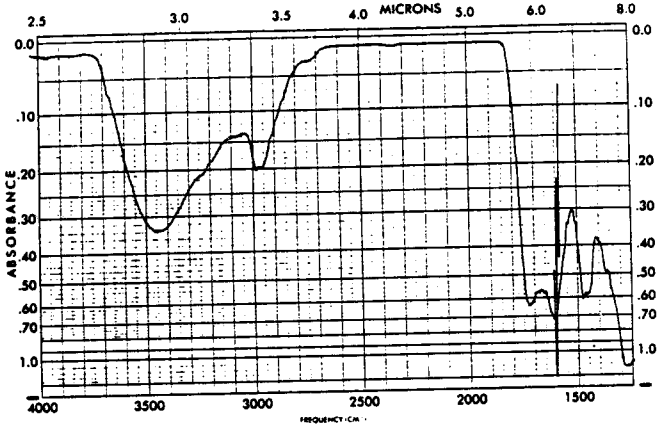


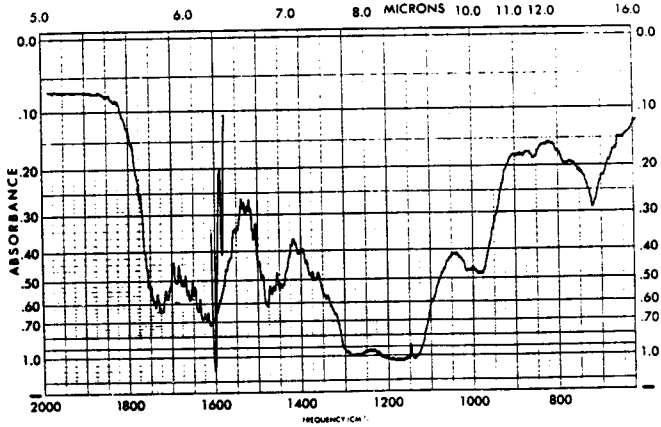
NMR spectrum of an unknown compound, reaction 13



A-21

Infrared spectrum of an unknown compound, reaction 14





UV/Visible spectrum of an unknown compound, reaction 14